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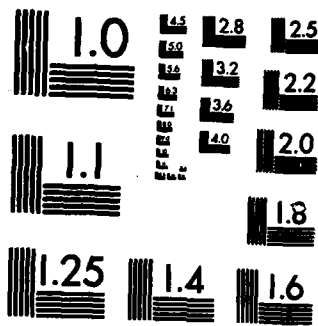
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TECHNICAL REPORT NO. 41

Ligand Structural Influences Upon Electrochemical
Reactivity: Organic Substituent Effects Upon
Carboxylatopentaamminecobalt(III) Reductions
at Mercury and Gold Electrodes

by

Tomi T-T. Li and Michael J. Weaver

Prepared for Publication

in the

Inorganic Chemistry

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January 1985

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 41	2. GOVT ACCESSION NO. A150 683	RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Ligand Structural Influences Upon Electrochemical Reactivity: Organic Substituent Effects Upon Carboxylatopentaamminecobalt(III) Reductions at Mercury and Gold Electrodes		5. TYPE OF REPORT & PERIOD COVERED Technical Report No. 40
7. AUTHOR(s) Tomi T-T. Li and Michael J. Weaver		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Purdue University West Lafayette, IN 47907		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0670
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 1985
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES CONT		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) ligand-surface interactions, substituent effects, nonaqueous media		
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Keywords include:

Originator Supplied

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LIGAND STRUCTURAL INFLUENCES UPON ELECTROCHEMICAL REACTIVITY:
ORGANIC SUBSTITUENT EFFECTS UPON CARBOXYLATOPENTAAMMINECOBALT(III)
REDUCTIONS AT MERCURY AND GOLD ELECTRODES

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ABSTRACT

The electroreduction kinetics of 33 carboxylatopentaamminecobalt(III) complexes containing a variety of aliphatic, aromatic, and heterocyclic substituents have been examined at mercury- and gold-aqueous interfaces and compared with the corresponding homogeneous reduction rates with $\text{Ru}(\text{NH}_3)_6^{2+}$ in order to examine the relationships between the substituent structure and electrochemical reactivity. Complexes having acyclic aliphatic groups yielded "normal" outer-sphere reactivities on the basis of their similar relative rate constants at a given electrode potential in comparison with the corresponding homogeneous rate ratios. However, electrochemical reactivities that are enhanced by ca 10 to 10^4 fold on this basis were observed for complexes with ring-containing substituents. The extent of these rate enhancements depended on the ring structure, the smallest (ca 10 to 30 fold) being seen with aliphatic ring substituents, and the largest (200 to 10^3 fold) for thiophenes, with intermediate values for reactants having furan, pyridine, and benzene groups. Similar unimolecular rate constants were nonetheless observed for the electroreduction of several of these complexes when electrostatically adsorbed at chloride-coated silver. This indicates that the observed catalysis at mercury and gold surfaces arises from reactant adsorption, i.e., from increased precursor stability, presumably associated with "hydrophobic" or van der Waals ligand-surface interactions. "Normal" outer-sphere electroreduction pathways were observed, however, at mercury electrodes in several aprotic solvents, as deduced from the common correlation between the electrochemical reactivities and the inductive substituent parameter. A similar correlation is seen for the $\text{Ru}(\text{NH}_3)_6^{2+}$ reduction kinetics in aqueous solution.

INTRODUCTION

We have recently been examining the kinetics of simple electrochemical reactions involving transition-metal systems, primarily Co(III)/(II), Cr(III)/(II), and Ru(III)/(II) couples at a variety of metal-solution interfaces.¹ One objective is to evaluate how the rates and mechanisms of heterogeneous electron-transfer reactions are influenced by the coordinated ligand structure, especially in relation to the detailed picture of reactant structural effects that has emerged for reactions between metal complexes in homogeneous solution.² Similarly to homogeneous processes, such electrochemical reactions commonly occur via inner-sphere mechanisms where a coordinated ligand is bound directly in the transition state for electron transfer.^{2a} Not surprisingly, the kinetics of such inner-sphere reactions are often extremely sensitive to both the nature of the metal surface and to the bridging ligand.^{1f-h,2c}

By analogy with homogeneous process, outer-sphere electrochemical mechanisms are anticipated for reactants that lack a functional group capable of binding to the metal surface. Thus electron transfer involving such species is expected to occur without the coordinated ligands penetrating the inner layer of solvent molecules adjacent to the electrode surface (the electrode's "coordination layer").^{2a} One therefore might expect that the reactant-electrode interactions for such pathways would be weak and nonspecific, such that the reaction energetics would be essentially unaffected by the interfacial environment.

A useful way of testing this notion is to examine the sensitivity of the electrochemical reactivities to variations in the ligand structure at a given electrode potential, E , in comparison with the corresponding relative homogeneous reactivities obtained using a fixed outer-sphere reducing (or

oxidizing) agent, $X^{1b,c,d,f,h,2b,c,3}$ Providing outer-sphere pathways are uniformly followed, we expect that⁴

$$(\Delta \log k_{\text{corr}}^e)_E = (\Delta \log k_{\text{corr}}^h)_X \quad (1)$$

where $\Delta \log k_{\text{corr}}^e$ and $\Delta \log k_{\text{corr}}^h$ are the corresponding variations in the work-corrected electrochemical and homogeneous rate constants, respectively. Although reasonable accordance with Eq. (1) has been found for a number of systems, substantial deviations have also been observed.^{1b,c,d,2b}

Of particular interest are the rate variations induced by the presence of organic substituents. We have found that the substitution of the aquo ligand in $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ by 4,4'-bipyridine and related nitrogen heterocyclic ligands yields substantial (up to 10^4 fold) enhancements of the Co(III) reduction rates at mercury-, platinum-, and gold-aqueous interfaces in comparison to their relative homogeneous outer-sphere reactivities, even though several of these ligands lack an effective surface binding group.^{1d} This behavior appears to be due to reactant adsorption induced by the relatively "hydrophobic" organic ligands.^{1d}

We have recently employed a variety of aromatic and aliphatic carboxylate ligands bound to pentaamminecobalt(III) and containing a sulfur surface binding group in order to examine the dependence of the unimolecular rate parameters for reduction of surface-attached Co(III) upon the structure of the extended organic bridging group.^{1h,2c,5} A valuable feature of such $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ reduction reactions is that wide variations in the extent of reactant-surface interactions can be achieved by altering remote substituents in the carboxylate ligand L, thereby maintaining the cobalt redox environment roughly constant. Such systems have received detailed attention in homogeneous solution.⁶ Not surprisingly, $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}$ complexes containing ligands

suitable for surface attachment, such as thiophenecarboxylates,^{1h} yield observed electrochemical rate constants, k_{ob} (cm sec^{-1}), that are typically $\text{ca } 10^3$ to 10^4 fold larger than for related reactants, such as $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ (OAc = acetate), that lack such binding groups.^{1h} However, we have also observed large values of k_{ob} for other $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}$ complexes at mercury and gold electrodes where L contains an extended organic functional group, such as furans,^{1h} that are not expected to bind strongly to these surfaces.

We describe here a systematic examination of the electroreduction kinetics of 33 $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes containing a variety of organic-substituted carboxylates, L, at mercury and gold electrodes. The aim is to ascertain broad relationships between the electrocatalytic properties (i.e., k_{ob} enhancements) and the structural features of L. Comparisons are presented between the electrochemical reactivities at mercury and gold electrodes and rate constants for the corresponding homogeneous reactions in aqueous solution with the outer-sphere reductant $\text{Ru}(\text{NH}_3)_6^{2+}$. Electrochemical rate data are also presented in dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), formamide, and propylene carbonate in order to examine further the influence of reactant-solvent interactions upon the reactivity patterns.

EXPERIMENTAL

Carboxylatopentaamminecobalt(III) perchlorates not available from previous studies^{1h,5} were prepared either from aquopentaamminecobalt(III) perchlorate in aqueous solution or from carbonatopentaamminecobalt(III) nitrate in diethyleneglycol by utilizing the procedures outlined in refs. 1h and 7, respectively. The carboxylate ligands were all obtained from Aldrich Co. Where necessary, the compounds were purified by chromatographic separation using Biogel P-2 anion resin, to remove unreacted ligand, eluted with water, and recrystallized from water. The purity was confirmed by elemental analysis and infrared and uv-visible spectra. Water was purified by using a Milli Q system (Millipore, Inc.). Sodium perchlorate supporting electrolyte (G. F. Smith) was twice recrystallized from water.

Most nonaqueous solvents (Burdick and Jackson, uv grade) were degassed and stored over molecular sieves before use. Tetraethylammonium perchlorate (G. F. Smith, Co.), used as the supporting electrolyte in nonaqueous media, was recrystallized twice from water and dried in a vacuum oven.

Most observed rate constants, k_{ob} (cm sec^{-1}), were determined as a function of electrode potential, E , at both dropping mercury and gold electrodes for ca. 1 mM reactant concentrations by means of normal pulse polarography using a PAR 174A Polarographic Analyzer as outlined in refs. 1a, 1g, and 1h. The gold electrode measurements utilized a rotating disk arrangement spun at 250-500 r.p.m. to eliminate the effect of reactant depletion from the preceding pulse.^{1g} Some rate constants were determined additionally by using either a.c. polarography or rotating disk voltammetry, the latter with rotation speeds between 100 and 2,000 r.p.m. The gold surfaces were pretreated as in ref. 1a. The resulting values of k_{ob} at gold were typically reproducible to $\pm 50\%$, whereas those at mercury could be reproduced to at least $\pm 20\%$.

Unimolecular rate constants, k_{et} (sec^{-1}), were obtained for some outer-sphere reactants by means of rapid linear sweep voltammetry, the complexes

being adsorbed electrostatically at halide-coated silver surfaces, as detailed in ref. 8, (see Results section). Second-order rate constants, k_{Ru} ($\text{M}^{-1} \text{sec}^{-1}$), for the outer-sphere reduction of the Co(III) complexes by $\text{Ru}(\text{NH}_3)_6^{2+}$ in homogeneous solution were determined using a polarographic method in 0.05 M sodium trifluoroacetate containing 5-20 mM trifluoroacetic acid as outlined in ref. 1h.

All electrode potentials are quoted with respect to the saturated calomel electrode (sce). All kinetic measurements were made at $24 \pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

Apparent Electrochemical Reactivities in Aqueous Media

Table I contains electrochemical rate constants, k_{ob} (cm sec^{-1}), and transfer coefficients, $\alpha_{\text{ob}} [= -(RT/F)(d \ln k_{\text{ob}}/dE)]$, for the one-electron reduction of thirty-three $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes (L = carboxylate) at mercury and gold electrodes in contact with aqueous 0.1 M NaClO_4 . A common electrode potential, -100 mV, is chosen so to facilitate intercomparison of the data; this value minimised the extent of $\ln k_{\text{ob}}-E$ data extrapolation. In any case, the relative rate constants are not greatly dependent on the electrode potential since the values of α_{ob} lie mostly in the range ca. 0.65-0.8 (Table I). Most rate measurements were made in solutions acidified to pH 2-3 with HClO_4 . Only small or negligible (two fold or less) values of k_{ob} were obtained using neutral media, even though several of the Co(III) complexes (in particular the nitrogen heterocycles⁹) are sufficiently strongly basic to be protonated even at pH 3. (For these systems, k_{ob} is slightly, up to 1.5-2 fold, larger in neutral media.)

All the Co(III) complexes were electroreduced in a single electron step, at least at potentials on the rising part of the polarographic or voltammetric waves, ca 100mV to -300mV, where the electrochemical kinetics could be obtained. Thus a well-defined diffusion-controlled current plateau was obtained in each case, corresponding to one-electron reduction with diffusion coefficients in the range $7 (+2) \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. This also indicates that the carboxylate ligands are not reduced under these conditions, either in coordinated or free form since they are released upon formation of Co(II). Indeed solutions containing the free ligands exhibited no electroreduction until potentials markedly more negative of -300mV.

The various substituents on the carboxylate ligands can be categorized as follows: (i) small acyclic aliphatic groups (systems 1-10); (ii) groups containing five- or six-membered aliphatic rings (systems 11-15); (iii) groups

containing benzene rings (systems 16-19); (iv) furan substituents (systems 20-22); (v) pyridine substituents (systems 23-26); (vi) thiophene substituents (systems 27-33). Of these ligands, (v) and (vi) contain heteroatoms (nitrogen and sulfur, respectively) that might be expected to bind to metal surfaces and therefore engender facile inner-sphere electroreduction pathways. The k_{ob} values for reduction of these reactants at mercury are indeed typically 10^2 - 10^3 fold larger than for those containing small aliphatic groups; this is reasonably attributed to such inner-sphere catalyses.^{1h} However, inspection of Table I reveals that large and even comparable electrochemical reactivities are also observed for reactants containing other alicyclic and aromatic substituents, especially benzene rings, that lack such surface "lead-in" groups.

These effects are illustrated more clearly in Fig. 1, which is a plot of $\log (k_{ob}^L/k_{ob}^{OAc})$, where k_{ob}^L and k_{ob}^{OAc} are the electrochemical rate constants for the reduction of a given complex and $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$, respectively, at mercury at -100 mV, against $\log (k_h^L/k_h^{OAc})$, where k_h^L and k_h^{OAc} are the corresponding rate constants for the homogeneous reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$. The reduction of $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ was selected as the "reference reaction" in view of the simple structure of the acetate ligand. Provided that the electrochemical, as well as homogeneous, reactions follow outer-sphere pathways, from Eq. (1) we expect that

$$\log (k_{ob}^L/k_{ob}^{OAc}) \approx \log (k_h^L/k_h^{OAc}) \quad (2)$$

since then the work-term corrections should be similar for each reaction and thereby cancel in the rate ratios.

Inspection of Fig. 1 reveals that reactants containing acyclic aliphatic [class (i)] substituents do yield good agreement with Eq. (2) in that almost all the points are close to the predicted straight line shown, having unit

slope and zero intercept. This suggests that these electrochemical reactions all proceed via similar, presumably outer-sphere, transition states (*vide infra*). However, the remaining points are uniformly above this line, so that the values of k_{ob} for all 24 reactants having ring-containing substituents [classes (ii)-(vi)] are between 20 and 10^3 fold larger than are expected from the homogeneous reactivities on the basis of Eq. (2). Some interesting trends can nonetheless be discerned from Fig. 1. Most prominently, the "degree of electrocatalysis" as measured by the vertical displacement of the experimental points above the "theoretical" solid line is systematically dependent upon the nature of the substituent ring. We shall express this electrocatalysis as the rate ratio k_{ob}^L/k_{ob}^{Eq2} , where k_{ob}^{Eq2} is the electrochemical rate constant corresponding to k_{ob}^L that is predicted from Eq. 2; i.e., from the straight line in Fig. 1. For the various substituent classes, the approximate range of values of k_{ob}^L/k_{ob}^{Eq2} are as follows: alicyclic aliphatics [class (ii)], 10-30; benzene substituents [class (iii)], 100-300; furans [class (iv)], 50; nitrogen heterocyclics [class (v)], 50-300; and for thiophenes [class (vi)], 10^2 - 10^3 . Of the class (i) substituents, only CCl_3COO^- yields a substantially higher electrochemical reactivity than predicted by Eq. (2) (Fig. 1).

The observed electrochemical rate constants can usefully be separated into precursor-state and electron-transfer contributions according to¹⁰

$$k_{ob} = K_p k_{et} \quad (3)$$

where K_p (cm) is the equilibrium constant for forming the precursor state (i.e., the reaction site in the double layer) from the bulk reactant, and k_{et} (sec^{-1}) is the unimolecular rate constant for the elementary electron-transfer step. The dependence of k_{et} as well as K_p upon the carboxylate

ligand structure has been scrutinized in detail for a number of thiophene-carboxylatecobalt(III) reductions occurring via thiophene-bridged transition states.^{1h} Substantially (ca. 10-20 fold) smaller values of k_{et} are found at mercury electrodes with bridging ligand containing one or more methylenes between the thiophene surface binding group and the cobalt compared to those for reactants with ligands featuring uninterrupted conjugation. These differences appear to be due to the occurrence of nonadiabatic pathways (i.e., where the electronic transmission coefficient $\kappa_{el} < 1$) for the former systems. For the latter, it appears that $\kappa_{el} \sim 1$; the reactivity enhancement, k_{ob}^L/k_{ob}^{Eq2} , for these inner-sphere systems relative to structurally similar outer-sphere reactions (such as $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ reduction) is due largely to the large (ca. 10^3 fold) increases in K_p resulting from surface attachment.^{1h}

Values of K_p at mercury were not determined directly for the other Co(III) carboxylate reactants in Table I since they are insufficiently large ($K_p \leq 10^{-4}$ cm) to be extracted reliably from rapid linear sweep voltammetry.^{1h} Nonetheless, broadly speaking, the variations of k_{ob}^L/k_{ob}^{Eq2} with the substituent ring structure noted above can also be rationalized in terms of differences in precursor stabilities (*vide infra*). Thus the presence of unsaturated rings [classes (iii)-(vi)] yields substantially larger k_{ob}^L/k_{ob}^{Eq2} values than for the aliphatic rings. This suggests that ring-metal surface π interactions and possibly "hydrophobic interactions" contribute importantly to the stabilization of the precursor state, although differences in κ_{el} , and hence in k_{et} , may also play a significant role. In particular, the observation that the k_{ob}^L/k_{ob}^{Eq2} values with the benzene substituents are close to those for the thiophene complexes implicates the importance of such aromatic rings to the precursor stability. The ca. 5-50

fold larger values of k_{ob}^L/k_{ob}^{Eq2} for the thiophene reactants relative to those found with the closely analogous furan substituents (Fig. 1); i.e., where the sulfur atom is replaced by oxygen, nevertheless illustrates the influence of the heterocyclic atom upon K_p , probably as a result of surface σ bonding.^{1h} Such effects also likely to be responsible for the ca. 20 fold larger value of k_{ob} for $L = CCl_3COO^-$ with respect to $L = CF_3COO^-$ (points 3 and 4, Fig. 1), presumably associated with chlorine-mercury surface interactions.

An alternative way of examining such ligand effects upon the redox reactivities involves their correlation with inductive and steric parameters for the various substituent groups.^{6b,11} Figure 2A is a plot of $\log k_{ob}$ for thirteen $Co(NH_3)_5L^{2+}$ electroreduction reactions against the Taft inductive parameter, σ^* , for each carboxylate substituent.¹² For the acyclic aliphatic substituents, $\log k_{ob}$ increases approximately linearly with increasing σ^* ; i.e., with increasing electron-withdrawal power of the organic substituent. Although the effect is relatively small, it is consistent with thermodynamic expectations since electron withdrawal from the cobalt redox center is expected to destabilize Co(III) relative to Co(II), shifting the (unknown) Co(III)/(II) formal potential positive and thereby increasing k_{ob} at a given electrode potential. A similar correlation is seen for the corresponding homogeneous reactivities, $\log k_h$, of $Co(NH_3)_5L^{2+}$ with $Ru(NH_3)_6^{2+}$ in Fig. 2B, even though some systems, for example $L = (CH_3)_3COO^-$, have k_h values that are somewhat smaller than expected. This may be due to the influence of steric effects associated with the electrostatically preferred approach of the $Ru(NH_3)_6^{2+}$ reductant to the negatively charged carboxylate ligand. This effect is, however, probably small for most systems in Fig 2B since addition of a suitably weighted term based on Taft steric parameter¹² does little to improve the correlation.

While a consistent $\log k_n - \sigma^*$ correlation is also observed for reactants with ring-containing as well as acyclic substituents (Fig. 2B), the former

yield electrochemical reactivities that are substantially larger than expected from the $\log k_{ob} - \sigma^*$ correlation (Fig. 2A). This provides further evidence that the unexpectedly large values of k_{ob} for alicyclic as well as aromatic substituents (Fig. 1) arise from the influence of the interfacial environment.

Unimolecular Electrochemical Reactivities

An additional means of examining the electrochemical reactivities of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes involves the direct evaluation of unimolecular rate constants, k_{et} , by means of rapid linear sweep voltammetry of electrostatically adsorbed reactant at halide-coated silver surfaces.⁸ Table II contains values of k_{et} determined in this manner at chloride-coated silver for the reduction of five $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes and also $\text{Co}(\text{NH}_3)_6^{3+}$ at -200 mV vs s.c.e. Full details of such measurements are given in ref. 8. The striking feature of the k_{et} values in Table II is that, similarly to the corresponding k_h values (Table I), they are virtually independent of the carboxylate ligand.

Such k_{et} values can also be employed to extract precursor stability constants, K_p , from the corresponding k_{ob} values obtained at the mercury-aqueous interface by using Eq. (3). It is preferable, however, to correct k_{et} for the double-layer potential drop, ϕ_r , at the silver surface, yielding a "work-corrected" value, k_{et}^{corr} , that would be observed at a given electrode potential if $\phi_r = 0$. (This value of k_{et}^{corr} can therefore be assumed to be roughly independent of the surface environment, and therefore appropriate for mercury as well as silver surfaces.) These quantities are related by⁸

$$k_{et}^{\text{corr}} = k_{et} \exp(-\alpha_{\text{corr}} F \phi_r / RT) \quad (4)$$

where the work-corrected transfer coefficient is approximated⁸ by $\alpha_{et} [= -(RT/F)(d \ln k_{et} / dE)]$ (Table II). For the present conditions,

$\phi_r = -110$ mV;⁸ the values of k_{et}^{corr} at -200 mV obtained from k_{et} by using Eq. (4) are also listed in Table II. These are combined with the corresponding k_{ob} values obtained at mercury electrodes at -200 mV to yield the "effective" precursor stability constants, K'_p , given in Table II by using

$$K'_p = k_{ob}/k_{et}^{corr} \quad (5)$$

[These precursor stability constants K'_p differ slightly from the values, K_p , defined by Eq. (3) in that the former contain an electrostatic component appropriate to the effective *transition-state* charge ($Z_r - \alpha_{corr}$), rather than to the reactant charge Z_r .¹³] It is useful to define a "nonelectrostatic" (or "statistical"¹⁰) component of K'_p , K_o , given by

$$K_o = K'_p \exp[(Z_r - \alpha_{corr})F\phi_r/RT] \quad (6)$$

where ϕ_r is now the reaction-site potential at the mercury-aqueous interface. The resulting estimates of K_o for the reactions at the mercury-aqueous 0.1 M NaClO_4 interface at -200 mV, assuming that $\phi_r \approx -20$ mV under these conditions,¹⁴ are listed in Table II.

For outer-sphere reactions, it is expected that¹⁵

$$K_o \approx \chi + (\sim 5 \times 10^{-9} \text{ cm}) \quad (7)$$

where χ is the distance beyond the plane of closest approach over which reaction adiabaticity is retained (i.e., for which the electronic transmission coefficient, κ_{el} , remains close to unity). The estimates of K_o for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ reduction in Table I, ca. 10^{-7} cm, are somewhat larger than that expected from Eq. (7), $K_o \sim 10^{-8}$ cm, given that we anticipate that $\chi \leq 1 \times 10^{-8}$ cm.¹⁵ This may be due to the inevitable uncertainties contained in the above analysis or, more likely, to a nonelectrostatic contribution

to K_o . However, the estimates of K_o for the ring-containing carboxylates in Table II are substantially (ca. 10^3 - 10^4 fold) larger than expected from Eq. (7), again implicating the presence of strong reactant adsorption arising from "specific" interactions between the substituent ring and the metal surface.

We have also observed facile electron mediation for Co(III) reduction by nitrogen heterocyclic ligands at mercury-, gold-, and platinum-aqueous interfaces.^{1d} These effects were similarly attributed to enhancement of the precursor stability via "hydrophobic" ring-surface interactions or π bonding. The present systems also display such behavior at the gold-aqueous interface. A plot of $\log (k_{ob}^L/k_{ob}^{OAc})$ at gold versus $\log (k_h^L/k_h^{OAc})$, similar to that shown for mercury electrodes in Fig. 1, is given in Fig. 2. Although a number of systems in the latter plot display considerably more scatter than in the former, the same general trends are observed in that most of the ring-containing reactants yield markedly enhanced reactivities compared with those predicted from Eq. (2). One apparent anomaly is that several of the thiophene-containing reactants display k_{ob} values that are not far from this prediction (i.e., close to the straight line shown), even though these reactants are very strongly adsorbed at gold.^{1h} This behavior is probably due to the occurrence of inhibited inner-sphere, or even outer-sphere, pathways under the d.c. voltammetric conditions where k_{ob} is measured arising from blockage of the electrode surface by irreversibly adsorbed reactant and the uncoordinated ligand product.

Electrochemical Kinetics in Nonaqueous Media

The foregoing demonstrates that strikingly large specific ligand effects can be induced on the electrochemical kinetics of even ostensibly outer-sphere reactions in aqueous solution. Inasmuch as reactant-solvent

and/or solvent-surface) interactions might be expected to play an important role, it is of interest to examine the corresponding ligand effects in nonaqueous media. Table III summarizes the electrochemical rate constants for reduction of four representative $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes with respect to that for $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ reduction at mercury, $k_{\text{ob}}^{\text{L}}/k_{\text{ob}}^{\text{OAc}}$, at a given electrode potential in four nonaqueous solvents as well as in aqueous solution. The electrode potentials for each solvent were chosen so to avoid data extrapolation. The electrolyte selected for the nonaqueous kinetic measurements was 0.1 M tetraethylammonium perchlorate (TEAP). (The values of $k_{\text{ob}}^{\text{L}}/k_{\text{ob}}^{\text{OAc}}$ were insensitive to the particular electrolyte chosen, as expected since the electrostatic work term embodied in Eq. (6) should be approximately the same for each reactant.)

The striking feature of the data in Table III is that the unexpectedly large values of $k_{\text{ob}}^{\text{L}}/k_{\text{ob}}^{\text{OAc}}$ for ring-containing substituents seen in aqueous solution are substantially diminished in nonaqueous media, especially in propylene carbonate, DMF, and DMSO within which hydrogen bonding is absent. Indeed, the values of $\log(k_{\text{ob}}^{\text{L}}/k_{\text{ob}}^{\text{OAc}})$ in these solvents correlate approximately with σ^* . This point is illustrated in Fig. 4, which is a plot of $\log k_{\text{ob}}$ versus σ^* for thirteen acyclic aliphatic and ring-containing reactants at the mercury-DMSO interface. In contrast to the corresponding plot for the mercury-aqueous interface (Fig. 3A), a unified correlation is obtained in Fig. 4 for all the reactions irrespective of the carboxylate substituent.

This strongly suggests that these aprotic solvents, in contrast to aqueous solution, engender "normal" outer-sphere pathways for electroreduction of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$, at least where L lacks a strongly surface binding group. This propensity for outer-sphere behavior in these aprotic media has also been seen for $\text{Co}(\text{en})_3^{3+/2+}$ electrochemical exchange (en = ethylenediamine),

whereas unexpectedly large standard rate constants were observed at the mercury-aqueous interface.¹⁶ The latter behavior also can be traced to a markedly enhanced value of K_o .⁸ Especially in the strongly "electron donating" solvents DMSO and DMF, the observed behavior can be understood in terms of the strong reactant solvation arising from specific ligand-solvent interactions involving the ammine hydrogens. These interactions exert important influences upon the redox thermodynamics.¹⁷ Presumably such strong solvation will hinder the close approach of the reactant to the metal surface. "Hydrophobic" interactions¹⁸ between the organic substituents and the surface, which probably aids reactant adsorption in aqueous solution, will be absent in aprotic media. (Indeed, the strong adsorption of a variety of organic molecules seen at metal-aqueous interfaces¹⁹ is largely absent from aprotic solvents.)

The presence of "abnormal" electroreduction pathways in aqueous solution is also suggested by the larger values of α_{ob} seen under these conditions compared to those in nonaqueous media (Tables I, III). Although complicated by diffuse-layer effects,¹⁴ these are suggestive of reaction sites closer to the electrode surface, as would be anticipated for reaction pathways featuring specific reactant-electrode interactions.

Concluding Remarks

The present results add substantially to the growing body of evidence indicating that substantial deviations from normal outer-sphere pathways often occur for mechanistically simple electrochemical reactions involving metal complexes in aqueous solution even when the coordinated ligands lack surface binding groups.^{1d,2d,8,16} These "surface environmental" effects can be very large, yielding up to ca. 10^4 fold alterations in k_{ob} . Broadly speaking, they are attributable primarily to variations in the

precursor stability associated either with specific ligand-surface interactions or with differences between the reactant-solvent interactions in the bulk solution and at the reaction site.^{1d} As noted in ref. 1d, one key difference between electrodes and homogeneous redox reagents is that the former always offer the possibility of delocalized reactant-surface interactions for reactants containing extended organic structural units.

Precursor structures involving π -interactions between substituent rings and the reductant have been postulated to occur for homogeneous reactions related to those considered here in order to account for unexpectedly large reactivities.²⁰ Another mechanism commonly proposed to account for enhanced homogeneous reduction rates involves sequential reduction of the organic ligand and the metal redox center.²¹ Similar pathways could also account for some enhanced electrochemical reaction rates with reactants containing reducible ligands. However, the impetus for such two-step pathways in competition with the alternative one-step mechanism presumably includes a diminution of the effective reorganization energy since the latter, but not the former, process necessarily involves simultaneous activation of both oxidizing and reducing redox centers. The electrochemical reductions, on the other hand, only involve reorganization of the oxidizing center since the metal surface "reductant" does not require nuclear activation. In any case, such ligand reduction pathways cannot account for the present results since as noted above the organic carboxylate ligands employed here do not undergo electroreduction in the potential range where the Co(III) reduction kinetics are monitored.

Nevertheless, the available evidence indicates that organic ligand effects upon electrochemical reactivities can be as striking as, if somewhat different from, those observed for homogeneous redox processes. The further

quantitative delineation of such effects, especially with parallel measurements of reactant adsorption, would be extremely worthwhile.

ACKNOWLEDGMENTS

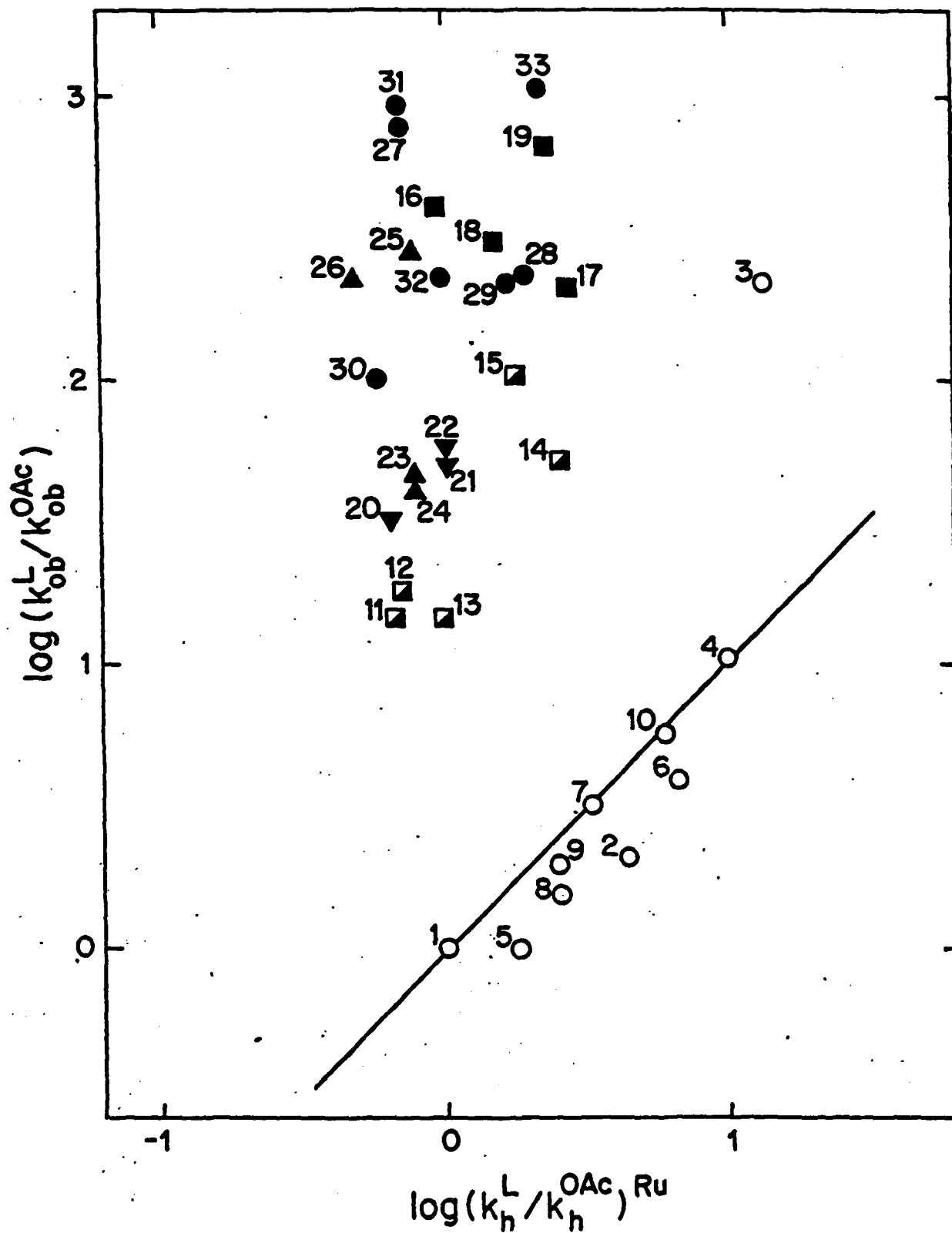
A number of initial experiments were performed by Drs. Seenu Srinivasan and Steve Barr. This work is supported by the Air Force Office of Scientific Research and the Office of Naval Research. M.J.W. acknowledges a fellowship from the Alfred P. Sloan Foundation.

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13. This is because k_{ob} is related to the corresponding "electrostatic work-corrected" rate constant, k_{corr} , at a given electrode potential by¹⁴
 $\ln k_{ob} = \ln k_{corr} - (Z - \alpha_{corr})F\phi / RT$; i.e., the work term correction is that appropriate to the effective transition state charge $(Z - \alpha_{corr})$ rather than Z . The corresponding relation between K_o and K_p^{corr} [cf. Eq. (6)] is^{8,10}
 $K_o = K_p^{corr} \exp(Z F \phi / RT)$.

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Fig 1



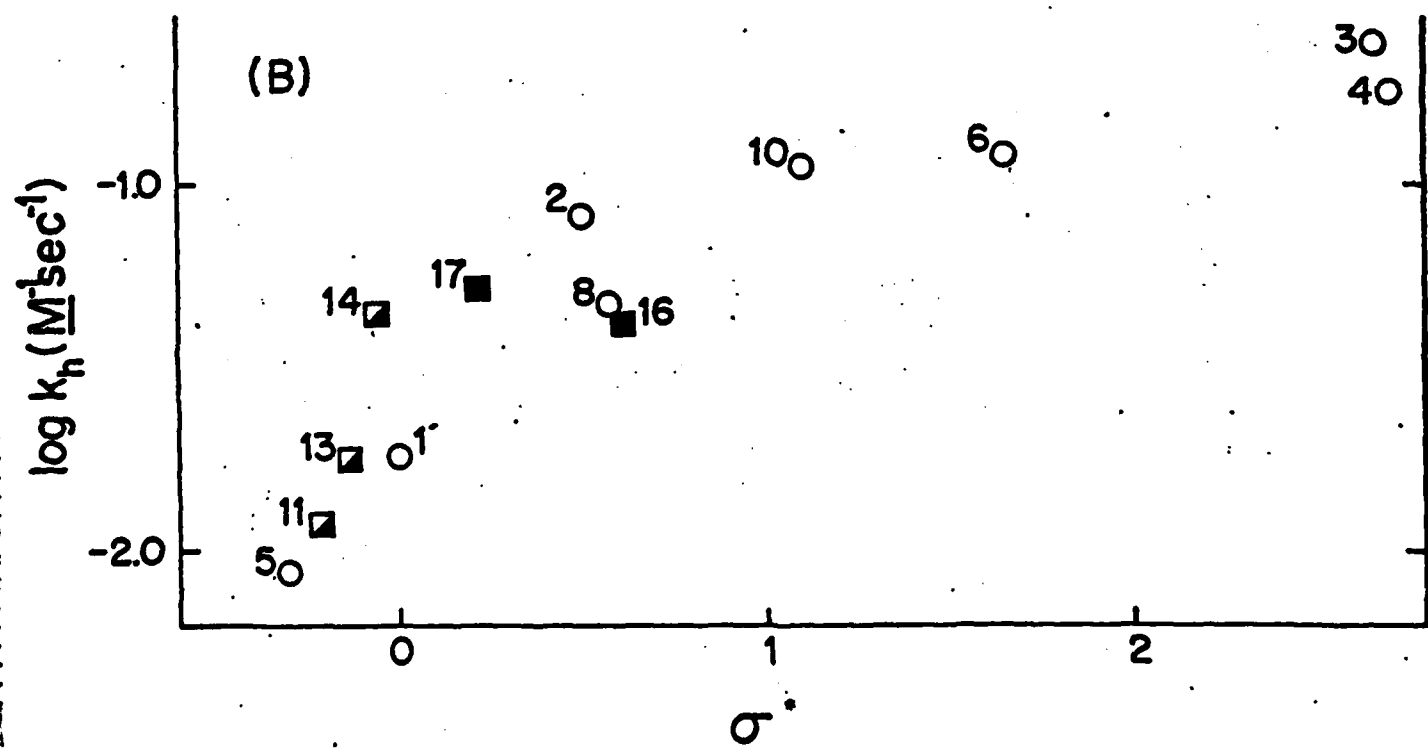
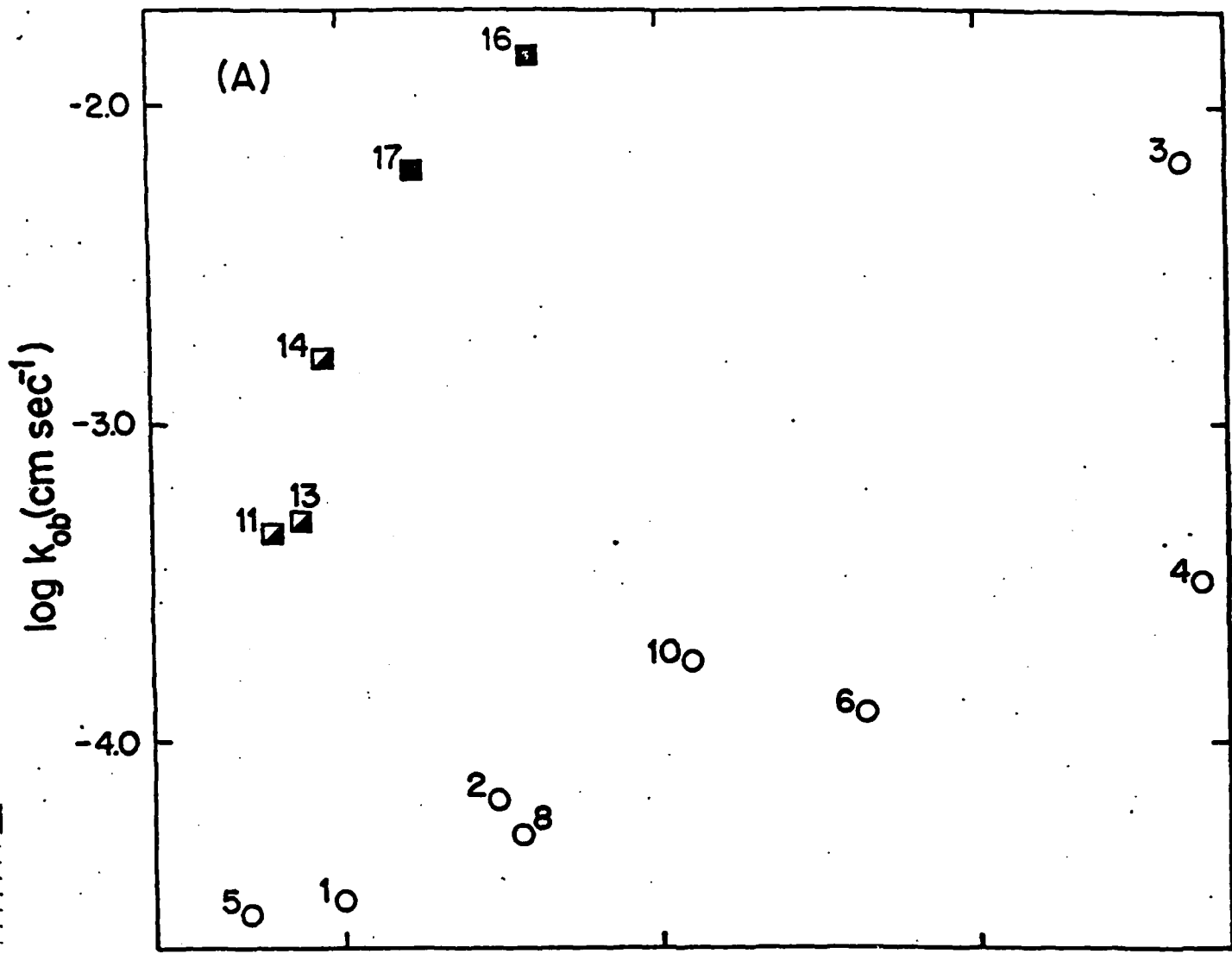


Fig 3

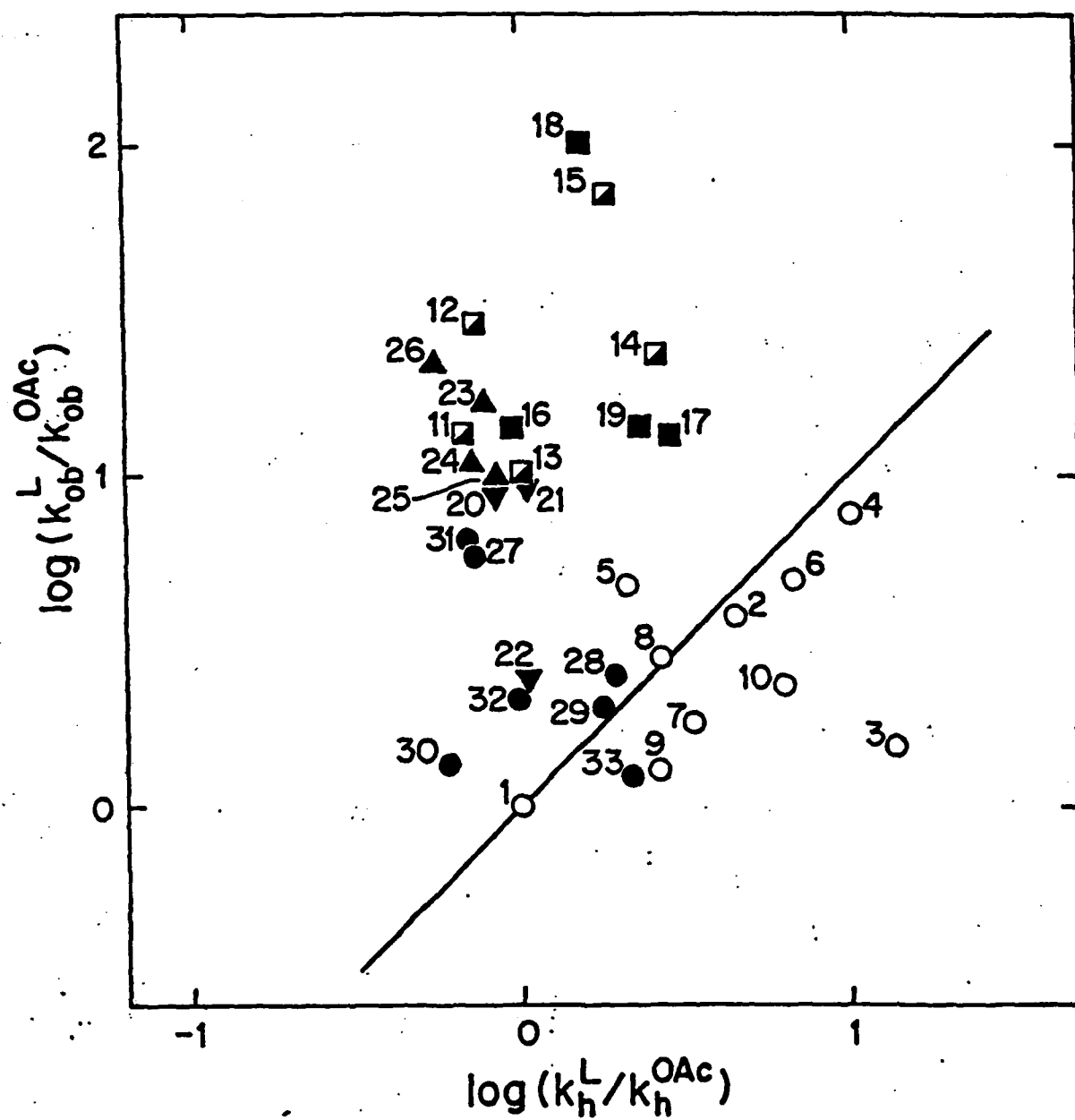


Fig 4

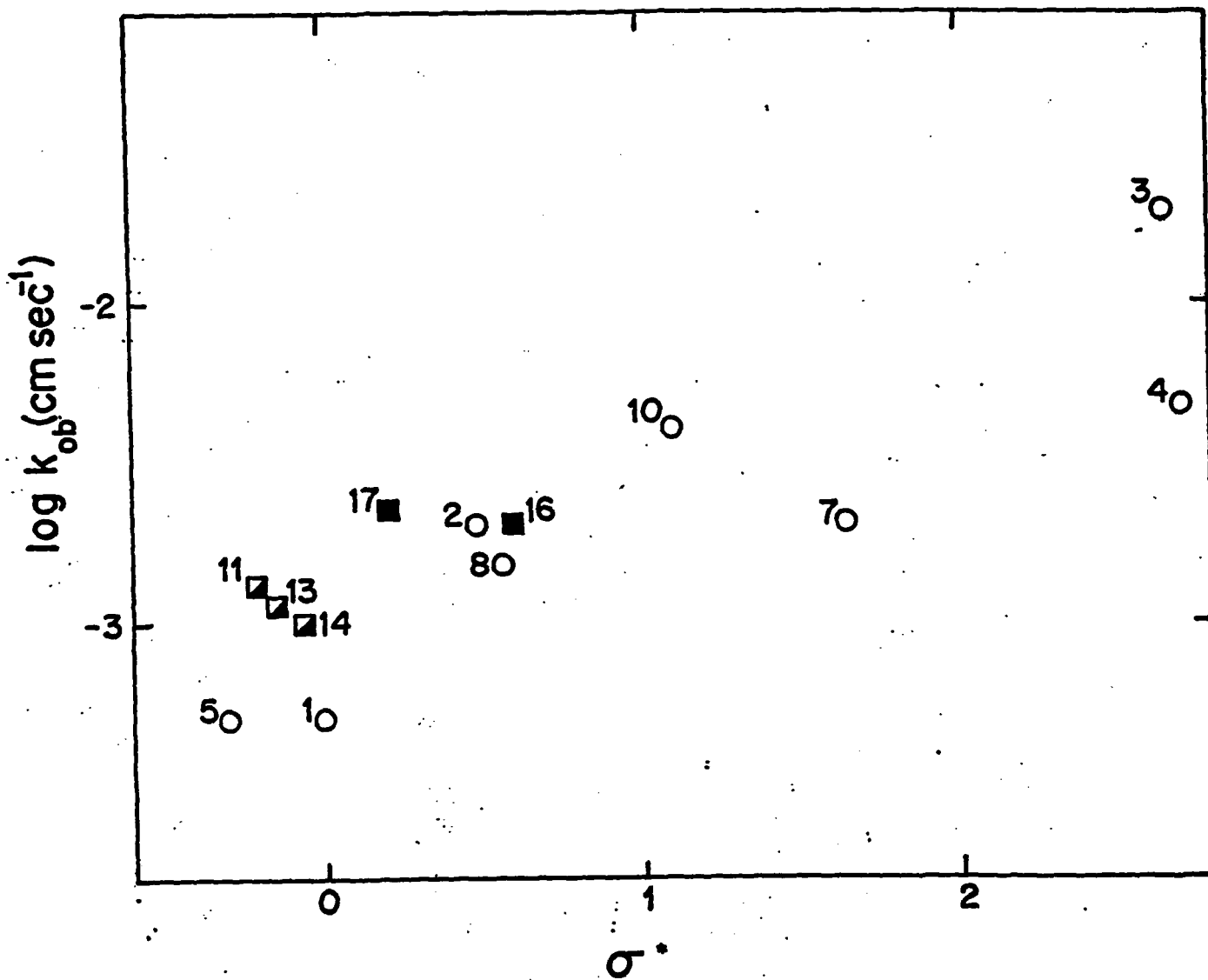


FIGURE CAPTIONS

Figure 1

Logarithm of ratio of rate constants, k_{ob}^L (cm sec^{-1}), for electroreduction of given $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complex with respect to that for $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$, k_{ob}^{OAc} , at mercury in aqueous $0.1 \text{ M NaClO}_4 + 5 \text{ mM HClO}_4$ at -100 mV vs sce , plotted against corresponding rate ratio, $\log(k_h^L/k_h^{\text{OAc}})$ for homogeneous second-order reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$ in aqueous 0.05 M sodium trifluoroacetate acid containing $5\text{--}20 \text{ mM}$ trifluoroacetic acid. Kinetic data detailed in Table I. Numbered points refer to system numbers given in Table I. Key to ligand types: (O) acyclic aliphatics, (◻) aliphatic rings, (■) benzene rings, (▼) furans, (▲) pyridines, (●) thiophenes.

Figure 2

Logarithm of rate constants for (A) electroreduction of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes at mercury and (B) homogeneous reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$ in aqueous solution plotted against Taft inductive parameter;¹² for key to system numbers see Table I, and for conditions and key to symbols see footnotes to Fig. 1.

Figure 3

As Fig. 1, but for electrochemical rate constants at gold-aqueous interface.

Figure 4

Logarithm of rate constants for electroreduction of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes at mercury-dimethylsulfoxide interface at -500 mV vs sce with 0.1 M tetraethylammonium perchlorate supporting electrolyte, plotted against Taft substituent parameter. See Table I for key to system numbers, and footnotes to Fig. 1 for key to symbols.

TABLE I. Rate Parameters for Reduction of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ Complexes at Mercury- and Gold-Aqueous Interfaces at -100 mV, and by $\text{Ru}(\text{NH}_3)_6^{2+}$ in Aqueous Solution.

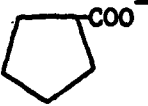
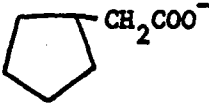
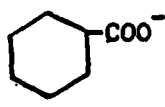
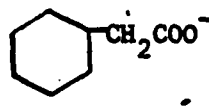
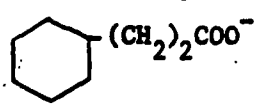
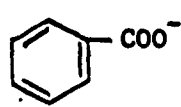
System No.	Ligand L	Mercury Electrode		Gold Electrode		$\text{Ru}(\text{NH}_3)_6^{2+}$ k_h $\text{M}^{-1} \text{sec}^{-1}$
		k_{ob}^a cm sec^{-1}	α_{ob}^b	k_{ob}^a cm sec^{-1}	α_{ob}^b	
1	CH_3COO^-	8.5×10^{-4}	0.58	3.1×10^{-5}	0.70	1.8×10^{-2}
2	HCOO^-	3.2×10^{-3}	0.52	6.5×10^{-5}	0.71	8.2×10^{-2}
3	CCl_3COO^-	4.2×10^{-2}	0.46	6.8×10^{-3}	0.73	2.5×10^{-1}
4	CF_3COO^-	6.5×10^{-3}	0.55	3.2×10^{-4}	0.67	1.8×10^{-1}
5	$(\text{CH}_3)_3\text{COO}^-$	4.0×10^{-3}	0.57	3.0×10^{-5}	0.66	8.7×10^{-3}
6.	$\text{CH}_3-\overset{\text{O}}{\parallel}\text{CCOO}^-$	4.0×10^{-3}	0.51	1.2×10^{-4}	0.52	1.2×10^{-1}
7.	$\overset{\text{O}}{\parallel}\text{HCCOO}^-$	1.5×10^{-3}	0.50	1.0×10^{-4}	0.52	5.9×10^{-2}
8.	$\text{CH}_2\text{OHCOO}^-$	2.4×10^{-3}	0.47	4.8×10^{-5}	0.66	4.7×10^{-2}
9.	$\text{CH}_3-\overset{\text{OH}}{\mid}\text{CHCOO}^-$	1.1×10^{-3}	0.50	6.0×10^{-5}	0.72	4.7×10^{-2}
10.	CH_2FCOO^-	2.0×10^{-3}	0.52	1.8×10^{-4}	0.70	1.1×10^{-1}
11.		1.1×10^{-2}	0.52	4.5×10^{-4}	0.77	1.2×10^{-2}
12.		2.5×10^{-2}	0.57	5.0×10^{-4}	0.77	1.3×10^{-2}
13.		8.5×10^{-3}	0.52	4.6×10^{-4}	0.77	1.8×10^{-2}
14.		2.0×10^{-2}	0.51	1.6×10^{-3}	0.74	4.6×10^{-2}
15.		6.1×10^{-2}	0.50	3.1×10^{-3}	0.70	3.3×10^{-2}
16.		1.0×10^{-2}	0.50	1.2×10^{-2}	0.65	1.7×10^{-2}

TABLE I Continued

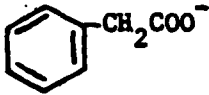
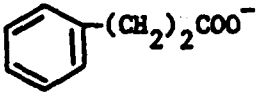
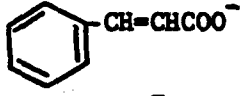
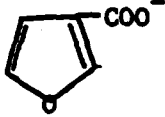
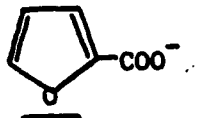
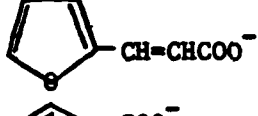
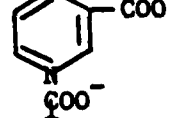
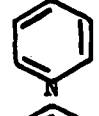
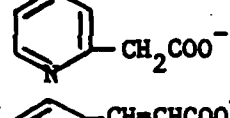

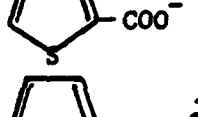
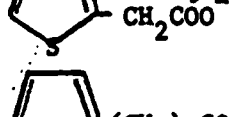
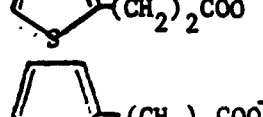
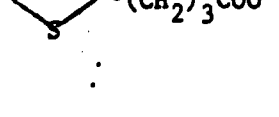
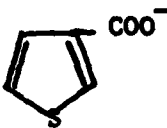
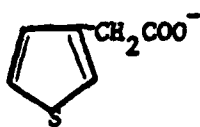
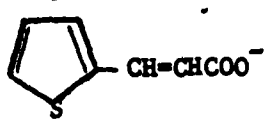
System No.	Ligand L	Mercury Electrode		Gold Electrode		$\text{Ru}(\text{NH}_3)_6^{2+}$
		k_{ob}^a cm sec^{-1}	α_{ob}^b	k_{ob}^a cm sec^{-1}	α_{ob}^b	k_h^c $\text{M}^{-1} \text{sec}^{-1}$
17		1.1×10^{-2}	0.55	6.5×10^{-3}	0.66	5.1×10^{-2}
18		8.7×10^{-2}	0.51	9.7×10^{-3}	0.64	2.8×10^{-2}
19		1.2×10^{-2}	0.51	2.0×10^{-2}	0.56	4.2×10^{-2}
20		7.4×10^{-3}	0.61	1.1×10^{-3}	0.83	1.2×10^{-2}
21		8.3×10^{-3}	0.55	1.5×10^{-3}	0.86	1.9×10^{-2}
22		2.1×10^{-3}	0.51	1.6×10^{-3}	0.53	1.9×10^{-2}
23		1.4×10^{-2}	0.56	1.5×10^{-3}	0.86	1.4×10^{-2}
24		1.0×10^{-2}	0.53	1.3×10^{-3}	0.85	1.3×10^{-2}
25		8.0×10^{-3}	0.51	8.9×10^{-3}	0.80	1.5×10^{-2}
26		1.9×10^{-2}	0.53	7.2×10^{-3}	0.87	1.0×10^{-2}
27		5.0×10^{-3}	0.75	2.3×10^{-2}	0.71	1.3×10^{-2}
28		2.1×10^{-3}	0.74	7.3×10^{-3}	0.75	3.5×10^{-2}
29		1.7×10^{-3}	0.65	7.0×10^{-3}	0.65	3.2×10^{-2}
30		1.1×10^{-3}	0.72	3.0×10^{-3}	0.57	1.1×10^{-2}

TABLE I Continued

System No.	Ligand L	Mercury Electrode		Gold Electrode		Ru(NH ₃) ₆ ²⁺
		k_{ob}^a cm sec ⁻¹	α_{ob}^b	k_{ob}^a cm sec ⁻¹	α_{ob}^b	k_h^c M ⁻¹ sec ⁻¹
31		5.2×10^{-3}	0.76	2.8×10^{-2}	0.72	1.3×10^{-2}
32		2.0×10^{-3}	0.71	7.5×10^{-3}	0.79	1.8×10^{-2}
33		1.1×10^{-3}	0.69	3.2×10^{-2}	0.62	4.1×10^{-2}




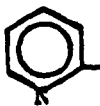
Footnotes to Table I

^a Observed rate constant for electroreduction of given Co(NH₃)₅L²⁺ complex at mercury or gold electrode, as indicated, at -100 mV vs sce in 0.1 M NaClO₄ + 5 mM HClO₄.

^b Observed transfer coefficient at mercury or gold electrode, as indicated, corresponding to listed value of k_{ob} .

^c Observed rate constant for homogeneous reduction of given Co(NH₃)₅L²⁺ complex by Ru(NH₃)₆²⁺ in aqueous 0.05 M sodium trifluoroacetate containing 5-20 mM trifluoroacetic acid.

TABLE II Unimolecular Rate Parameters for Outer-Sphere Reduction of $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{L}$ Complexes at -200 mV vs sce at Chloride-Coated Silver-Aqueous Interface. Comparison with Corresponding Rate Parameters for Aqueous Solution Reactants at Mercury Electrodes.

Ligand L	k_{et}^a sec ⁻¹	α_{et}^b	$k_{\text{et}}^{\text{corr}c}$ sec ⁻¹	k_{ob}^d cm sec ⁻¹	α_{ob}^e	K_p^f cm	K_o^g cm
NH_3	20	0.68	4×10^2	2.5×10^{-4}	0.7	6×10^{-7}	8×10^{-8}
CH_3COO^-	15	0.7	3×10^2	3.5×10^{-4}	0.7	1.2×10^{-6}	3×10^{-7}
 - COO^-	15	0.7	3×10^2	8×10^{-3}	0.75	3×10^{-5}	8×10^{-6}
 - COO^-	20	0.65	4×10^2	0.15	0.65	3.5×10^{-4}	1×10^{-4}
 - COO^-	50	0.75	1×10^3	3.5×10^{-2}	0.8	3.5×10^{-5}	1×10^{-5}
 - CH_2COO^-	15	0.7	3×10^2	0.2	0.8	6.5×10^{-4}	2×10^{-4}

^aUnimolecular rate constant for electron-transfer step at -200 mV, determined by means of rapid linear sweep voltammetry for electrostatically adsorbed reactant at silver electrode in 0.1 M KCl as outlined in ref. 8.

^bTransfer coefficient for electron-transfer step, determined as in footnote (a).⁸

^cWork-corrected unimolecular rate constant at -200 mV, estimated from k_{et} by correcting for potential at reaction plane at chloride-coated silver^{et} (≈ -110 mV) (see text and ref. 8).

^dObserved rate constant for solution reactant at -200 mV at mercury electrodes in 0.1 M NaClO_4 (pH 2.5) determined by using normal pulse polarography.

^eObserved transfer coefficient for solution reactant, corresponding to k_{ob} .

^fPrecursor stability constant, determined from Eq. (5).

^gElectrostatic-corrected precursor stability constant, determined from K_p by using Eq. (6), with $\phi_r = -20$ mV (see text).

TABLE III Relative Electrochemical Reactivities, k_{ob}^L/k_{ob}^{OAc} , and Transfer Coefficients, α_{ob}^L , for Reduction of $Co(NH_3)_5L$ Complexes at Mercury Electrodes in Various Solvents.

System ^c No.	Ligand L	σ^d	Water k_{ob}^L/k_{ob}^{OAc} α_{ob}^L	Propylene Carbonate k_{ob}^L/k_{ob}^{OAc} α_{ob}^L	Formamide k_{ob}^L/k_{ob}^{OAc} α_{ob}^L	DMF k_{ob}^L/k_{ob}^{OAc} α_{ob}^L	DMSO k_{ob}^L/k_{ob}^{OAc} α_{ob}^L
1	<chem>CH3COO-</chem>	0	(3.1×10^{-5}); 0.70 -100 mV	(1.6×10^{-3}); -200 mV	(1.3×10^{-3}); 0.74 -500 mV	(4.4×10^{-3}); 0.56 -500 mV	(5×10^{-3}); 0.52 -500 mV
13	<chem>C1CCCCC1C(=O)[O-]</chem>	-0.15	15 0.77	0.6	2.7 0.68	2.7 0.61	0.22 0.50
16	<chem>c1ccccc1C(=O)[O-]</chem>	+0.6	4×10^2 0.65	2.4	7.7 0.65	2.5 0.66	2.0 0.51
21	<chem>c1ccccc1C(=O)[O-]</chem>	-	50 0.86	3.1	5.5 0.68	1.4 0.61	1.5 0.54
23	<chem>c1ccc(C(=O)[O-])cc1</chem>	-	50 0.85	2.4	11.5 0.65	2.6 0.57	2.2 0.50

^aElectrochemical rate constant for reduction of given $Co(NH_3)_5L^{2+}$ complex, k_{ob}^L , with respect to that for $Co(NH_3)_5OAc^{2+}$, k_{ob}^{OAc} , at given electrode potential, measured in 0.1 M tetraethylammonium perchlorate (TEAP) in nonaqueous media and in 0.1 M NaClO₄ in aqueous solution. Value of k_{ob}^{OAc} (cm sec⁻¹) in each solvent, together with electrode potential (mV vs. aqueous sce) at which it is measured, given in parenthesis in first row.

^bMeasured in some electrolytes as those noted for k_{ob}^L in footnote (a).

^cSystem numbers as in Table I.

^dTaft inductive parameter for given carboxylate substituent, from ref. 12.

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